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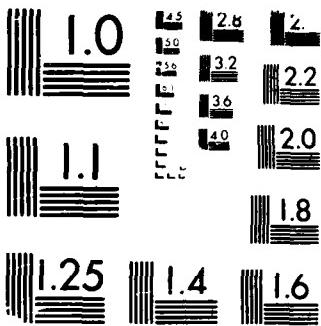
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TRANSPORT OF ORGANIC VAPORS IN
MULTIPHASE POLYMER SYSTEM

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FINAL TECHNICAL REPORT

NAK-HO SUNG AND JERRY H. MELDON

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) Sorption of organic vapors in glassy-rubbery heterophase polymers is investigated using polystyrene (PS)/Polybutadiene (PB) blends and block copolymers. Experimental data on hexane vapor sorption in phase segregated blends (mixture of dispersed PS microspheres in PB matrix) and block copolymers exhibit non-Fickian characteristics that previous workers with PS/PB copolymers attributed to a diffused interphase. These data, plus results from a model of sorption in heterogeneous media containing a slowly permeable dispersed phase, indicate that the mere presence of two phases with different diffusion time constants is a sufficient condition for apparently non-Fickian behavior. A mold of vapor transport in glassy polymer is presented and employed in conjunction with sorption experiments with PS microspheres in order to determine pertinent diffusion and relaxation constants. The same model and parameters are incorporated into a model of transport in heterophase polymers in an attempt to stimulate experimental measurements of hexane uptake in PS/PB blends. The fit to sorption data in pure PS microspheres and PS/PB blends is mostly qualitative due to the complexity of glassy phase transport					
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A. BACKGROUND

There are numerous applications in which solvent permeation characteristics determine material selection for protective films and coatings, and protective wear. Transport in heterophase polymers, containing both glassy and rubbery, is, however, poorly understood because of the variety of factors, both chemical and structural, which govern the dynamics and equilibrium of penetrant uptake. There is a need for a fundamental understanding of penetrant uptake and transport in relation to the nature and dimensions of the rubbery and glassy phases, and the phase segregation at the interface between the two. Also, a theoretical analysis is needed to better define the influences upon transport, of the permeation characteristics and dimensions of hard and soft domains.

B. SUMMARY OF RESULTS

The research undertaken with A.R.O. support was directed at elucidating the mechanism of organic vapor transport in heterogeneous polymer films. In particular, the work aimed to develop a working mathematical model of transient diffusion of solvent vapors in composite films, cast in the form of a flat sheet, and composed of a mixture of glassy and rubbery domains. Transient diffusion was to be examined in light of the fact that the majority of experimental work reported in the preceding years consisted of measurements of the rate of uptake of solvent vapor in a slab of polymer, following a step increase or decrease in solvent activity.

It was realized at the start that it would be necessary to compare our theoretical model's predictions, with the results of experiments performed in our laboratory under well-defined conditions. In particular, the morphology of heterophase polymer samples had to be well-characterized. To this end, we chose to work with composite blends made up of glassy polystyrene (PS) or microspheres dispersed within a continuous matrix of rubbery polybutadiene (PB). These two polymers were selected because of the extensive prior work with PS/PB systems, both as blends and copolymers. Furthermore, n-hexane was selected as the solvent vapor on the similar grounds that substantial and apparently reliable work had previously been undertaken with hexane and the two polymers, both as homo- and heteropolymer systems.



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Thus, the experimental program consisted primarily of measurements of the rate of uptake of hexane vapor by: a) thin slabs of polybutadiene, b) microspheres of polystyrene, and c) composite blends of PS in PB. The transient data indicating rate of sorption were ultimately compared with the mathematical models developed in parallel. Equilibrium data, i.e., weight fraction solvent vs. solvent activity, were used to trace out sorption isotherms. Data obtained for the respective pure PB and PS samples were used in order to predict the experimental results with blends.

In addition, to the aforementioned primary project, additional experimental work was undertaken with PS/PB block copolymers with various solvent penetrants. This complementary data served to highlight differences in sorption behavior when the two polymers are chemically linked (vs. the non-linkage in the primary model system).

It should be noted at the start that the apparent conventional wisdom at the commencement of this project was that, during transient hexane uptake by polybutadiene/polystyrene blends and copolymers, there is negligible hexane uptake by the polystyrene domains per se. Rather, two-stage sorption behavior was believed indicative of the slow uptake of solvent vapor by a diffuse PS/PB interphase the diffusion and solubility characteristics of which are presumably intermediate between those of the pure polymer domains. As will be noted below, the results of the present study suggest strongly that one cannot a priori neglect vapor uptake in glassy polystyrene domains. Our results demonstrate that the solubility of hexane in PS is appreciable. Furthermore, despite the fact that the diffusivity of hexane in glassy PS is indeed orders of magnitude lower than it is in rubbery PS, the fact that PS domains may themselves be orders of magnitude smaller than PB domains can be responsible for substantial PS uptake of hexane during transient experiments - e.g., during the time it takes for the continuous PB matrix to equilibrate with a step change in vapor activity.

In the initial stage of this project, an emulsion polymerization technique was applied successfully to the production of spherical polystyrene particles of diameters in the range 500 Angstroms to 10^4 Angstroms (= 1 micron). It was vital that microspheres of this size range be available for study, in view of the intrinsically low diffusivities of gases and vapors in glassy polymers. Even with microspheres in this small size range, equilibration times in sorption experiments could be of the order of one month.

Sorption experiments were undertaken with n-hexane vapor undergoing a step change in activity from zero to 0.4 (=the ratio of its pressure as a pure vapor to its vapor pressure at the experimental temperature of 25°C; the operating hexane pressure at this activity was ca. 60 torr). Experiments were undertaken both with glassy PS microspheres and flat sheets of PB of thickness of the order of 0.2 mm.

Sorption behavior in rubbery PB was, as anticipated, "Fickian." That is, the results could be fit with the known solution to Fick's second law, and when plotted as (fractional uptake) vs. (square root of time/thickness) were independent of thickness. Moreover, an excellent fit to the experimental data was obtained with a constant value of the hexane diffusion coefficient.

Sorption behavior in glassy PS was, on the other hand, and also as anticipated, distinctly non-Fickian. This was most pronouncedly revealed by the non-overlap of curves plotted on the same coordinates as those described in the previous paragraph, when those results were obtained in experiments subject to identical conditions except for microsphere diameter. Moreover, these results were not only size-dependent, but also varied with prior treatment (e.g., annealing and the presence or absence of surfactant in the casting solution). The results with any one microsphere diameter could not be fit with the known solution of Fick's second law in spherical coordinates, with a single, constant diffusion coefficient. However, as the diameter was increased, the ability to fit the data with a Fickian model improved.

The results with glassy PS were consistent, overall, with the voluminous data reported in recent years on vapor uptake by glassy polymers. Previous authors have generally interpreted the non-Fickian behavior to be a manifestation of the slow relaxation of polymer chains in response to a changing environment. This was taken into account in the development of a theoretical model of diffusion in glassy polymers, along lines laid out by previous investigators, which will be described below.

In parallel with the experimentation with pure polymer samples, composite PB/PS samples were prepared by solvent casting. As observed by earlier investigators who examined such heteropolymer systems, two-stage sorption behavior prevailed. Most significantly, the temporal segregation of the two stages was more pronounced when the size of the glassy PS microdomain increased relative to over all composite thickness. This was achieved in our study by employing microspheres of increasing size. Earlier workers had

simply cast thinner or thicker composite slabs. Our results were consistent with those of earlier workers in that Fickian behavior appeared to be the limiting one in the case of very thick overall sample sizes compared to glassy microdomain dimensions.

As a first theoretical analysis, we examined transient permeation with immobilizing chemical reaction. Chemical reaction was modelled in an analogous manner to adsorption or hole-filling, i.e., processes akin to those employed to model diffusion in glassy polymers in the Dual Sorption model adopted by several contemporary investigators. Since the chemical reaction investigated was first-order-reversible, the kinetics were identical to those assumed by these earlier authors. Our results indicated the importance of allowing sufficient experimental time for steady-state to be achieved in permeation runs. This was because of the prevalence of a pseudo-steady-state, followed by a later true steady-state, in a process with two time constants - one for diffusion and one for the immobilizing chemical reaction/adsorption/hole-filling process. When the latter process is much slower, there is a slow approach to the ultimate steady-state flux. That steady-state flux, interestingly, is the same flux as that achieved in the intermediate steady-state. The importance of being aware of the dual-steady state behavior lies in the use of transient permeation results to derive a value for the effective diffusion coefficient. This technique, based on the "time lag" associated with the approach to steady-state, will yield two different diffusion coefficients, depending on whether the intermediate or true steady-state flux is applied. In fact, only the higher diffusion coefficient obtained from the earlier steady-state describes the steady-state behavior. This is due to the fact that the steady-state flux is unaffected by the immobilizing process.

The next theoretical model developed was directed at transient permeation or sorption in heterophase systems. The sorption results would be used to rationalize our own experimental data. As already noted, our data and those of earlier workers establish the two-stage non-Fickian behavior of sorption in heterophase systems. Our first heterophase model examined the case of a two-phase system in which the diffusion behavior was Fickian in each phase. However, since diffusion in one phase could be much slower than in the other, the overall behavior was indeed non-Fickian. Thus, it was possible to produce theoretical curves that qualitatively mimicked experimental data for solvent vapor sorption in PS/PB composites. Notably, this was

achieved without resort to either an interphase hypothesis or the assumption on intrinsically non-Fickian behavior in one of both phases. However, as described below, it was impossible to achieve a quantitative fit to experimental data with this primitive model.

The experimental results for hexane sorption in PS/PB composites were extended to examine changes in behavior as the overall film thickness was varied, with a fixed size of PS microsphere. The results, like those described earlier in which the film thickness was fixed while the microsphere diameter was varied, and those of earlier workers, indicated more pronounced two-stage behavior when the microsphere diameter was higher rather than smaller, relative to overall thickness. This confirmed that sorption is governed by (at least) two processes differing in their time constants, and that the time constant on one such process varied with film thickness (or microsphere diameter).

Because the original heterophase transport model did not, however, allow quantitative fit to this experimental data, it was deemed necessary to develop a model of sorption in glassy PS microspheres. A model was developed along the lines described above for the analysis of permeation. In fact, the mathematical representation differed only in the substitution of sorption for permeation boundary conditions, with the same differential equations as were employed to represent diffusion with immobilization. Since this model amounted, once again, to a case involving two time constants - one for diffusion, one for immobilization - the resulting sorption behavior again exhibited temporal segregation of two phases. This was observed, again, when diffusion distances, i.e., microsphere diameters, were sufficiently small that diffusion equilibration was achieved prior to the onset of substantial immobilization/relaxation. This was indeed consistent with our experimental results, and those of earlier investigators of glassy polymer behavior. However, it was not possible to obtain quantitative fit to our experimental data for hexane sorption in PS microspheres, except in samples sufficiently thick that the behavior approached the Fickian.

The diffusion coefficients, on the other hand, that were derived from the Fickian uptake of hexane by rubbery polybutadiene, were consistent with earlier reports. Diffusion coefficients were consistent with Fujita's free volume theory, and sorption isotherms with the Flory-Huggins equation involving a single polymer/solvent interaction parameter (constant as solvent

activity varied). The effective mutual diffusion coefficient went through a maximum at 12% hexane concentration. Data for hexane in rubbery polystyrene, however, could not be rationalized by free volume theory.

Incorporation of the improved model of transport in glassy domains, into the heterophase model, did improve the fit to data obtained with composites. The necessary parameters were obtained from the experiments with the pure homopolymers. However, because even the improved glassy model did not allow a quantitative fit to the pure PS data, it was not surprising that insertion of the same parameters into the heterophase model similarly did not produce a quantitative fit to the composite data. On the one hand, a heterophase model that incorporates a glassy phase model with diffusion and relaxation, allows more parametric variation, since there are now three time constants - two for diffusion and one for relaxation. On the other hand, the true behavior in the glassy phase is apparently governed by at least two relaxation times. Thus, a single relaxation model could only qualitatively fit the data.

In addition to this work, separate, parallel projects were undertaken to characterize solvent vapor transport in heterophase polymer systems consisting of PS/PB block copolymers. Sorption of hexane, heptane, and cyclohexane in Kraton 1102 rubber, containing 28% of styrene domain in dispersed rods, is pseudo-Fickian lacking the thickness scaling. Solprene 414P, containing 40% of styrene domain in alternating lamellae with butadiene domain, and Kraton 1102 with 16% of added polystyrene (M.W.=230,000) thus making a total styrene to be 40%, both showed distinctive two-stage sorption behavior. The relative time scale of sorption in PS and PB domains, which is influenced by the structure and size of PS domains, is believed to be responsible for the two-stage behavior. The relaxation contribution of the PS domains to the two-stage behavior is considered negligible.

On the basis of this work, several conclusions can be drawn:

- 1) Transport behavior in heterogeneous polymer systems can apparently be explained without resort to hypothesizing a diffuse interphase with properties intermediate between those of the homopolymers;
- 2) Transport of hexane in PS/PB composites can involve substantial hexane uptake by glassy PS domains, despite orders of magnitude lower diffusion coefficients in PS, when the PS domains are appropriately smaller than the

characteristic dimension of rubbery domains;

- 3) Transport behavior of cyclohexane in PS/PB block copolymers ranges from pseudo-Fickian to two stage sorption largely due to relative time scales of sorption in glassy and rubbery domains, which is influenced by morphology of PS domains.
- 4) For the purpose of quantitatively modelling diffusion in glassy polystyrene, a model more sophisticated than ours, with a single relaxation time, is necessary. Accordingly a successful model of heterophase transport, i.e., in glassy/rubbery polymer composites, requires a similarly advanced model of transport in glassy polymers.

C. LIST OF PUBLICATIONS

1. "Analysis of Transient Phase Permeation with Immobilizing Chemical Reaction", I. & E.C. Fundamentals, 24, 61 (1985).
2. "Sorption and Diffusion Behavior of Styrene-Butadiene Block Copolymers", ACS PMSE 53, 325 (1985).
3. "Transient Permeation and Sorption in Heterogeneous Polymer Media", Poly. Eng. Sci., 26, 1045 (1986).
4. "Analysis of Diffusion Behavior in Glassy Polymers", submitted to J. Poly. Sci. Physics Ed. (1988).
5. "Vapor Sorption in a Heterophase Polymer Membrane", to be submitted to Macromolecules (1988).

D. PRESENTATIONS AT THE NATIONAL AND INTERNATIONAL MEETINGS

1. "Analysis of Transient Permeation and Sorption in Heterogeneous Media", American Institute of Chemical Engineers (AIChE), Annual Meeting, San Francisco, November 1984.
2. "Organic Vapor Sorption in Heterophase Polymer Membrane", Amer. Physical Society (APS), Annual Meeting, Baltimore, April 1985.
3. "Sorption and Diffusion Behavior of Styrene-Butadiene Block Copolymers Amer. Chemical Society (ACS), Annual Meeting, Chicago, September 1985.
4. "Vapor Sorption in Heterogeneous Polymers", APS Annual Meeting, Las Vegas, March 1986.

5. "Vapor Sorption in Heterophase Polymer Membranes", AIChE Annual Meeting, New Orleans, April 1986.
6. "Diffusion of Organic Vapors in Heterophase Polymer Membranes", Polymer Science and Plastics Technology Symposium, Sturbridge, MA, March 1988.

E. THESIS

1. "Effects of Morphology on the Sorption and Diffusion Behavior of Styrene-Butadiene Block Copolymers, by Christopher L. Mirley, M.S. Thesis in Chemical Engineering, June 1985.
2. "Sorption Behavior of n-Hexane in Glassy Polystyrene Microspheres; Surfactant and Size Effect", by Stavroula Poulou, M.S. Thesis in Chemical Engineering, November 1985.
3. "Diffusion of Organic Vapors in Glassy and Heterophase Polymer Systems", by Yong-Soo Kang, Ph.D. Dissertation in Chemical Engineering, May 1986.
4. "Sorption in Glassy Anomaly in Organic Vapor Microspheres", by Hyung J. Paik, M.S. Thesis, (to be completed in June 1988).
5. "Vapor Sorption in National Rubber of Varying Carbon Black Content" by Larry Waksman, M.S. Thesis (to be completed in June 1988).

F. LIST OF PERSONNEL INVOLVED IN PROJECT

Prof. Nak-Ho Sung, P.I.

Prof. Jerry H. Meldon, Co-P.I.

Dr. Yong-Soo Kang, Ph.D. 1986

Ms. Stavroula Poulou, M.S. 1985

Mr. Christopher L. Mirley, M.S. 1985

Mr. Hyung J. Paik, M.S. (to be completed in June 1988)

Ms. Lisa Winsor

*(Mr. Bruce Rosen)

*(Mr. Larry Waksman)

*Coop students working at the U.S. Army Materials Technology Laboratory, Watertown, MA.

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